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Study Leading to the Development of Polymers for Use
in High Temperatures

by

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Table of Contents

I. <u>Abstract</u>	1
II. <u>Reactions of the Dialkylamides of Trichlorophosphazosulfuric Acid with Grignard Reagents</u>	2
III. <u>Reactions of Bis-trichlorophosphazosulfone and of the Dialkylamides of Trichlorophosphazosulfuric Acid with Aliphatic Polyamines</u>	3
IV. <u>Physical Properties</u>	3
V. <u>Experimental</u>	4
VI. <u>Discussion</u>	5
VII. <u>Outline of Future Work</u>	6
VIII. <u>References</u>	6

I. Abstract

Reactions of the dialkyleamides of trichlorophosphazosulfuric acid with organo-metallic compounds have been continued during this synthesis period in an attempt to establish whether steric effects might be involved in these nucleophilic substitutions. Experiments thus far completed indicate this to be the case, inasmuch as completely substituted products with *m*-tolylmagnesium bromide are obtained only in very low yields, whereas with the *o*-tolyl Grignard they are practically non-existent.

Some reactions of bis-trichlorophosphazosulfone and of the dialkyleamides of trichlorophosphazosulfuric acid with aliphatic polyamines, with the object in view of obtaining organic-inorganic polymeric products, have been under investigation also.

II. Reactions of the Dialkylamides of Trichlorophosphazosulfuric Acid with Grignard Reagents

Complete replacement of the chlorine atoms in bis-trichlorophosphazosulfone and in the dialkylamides of trichlorophosphazosulfuric acid by various Grignard reagents has been fully described in a previous report (1).

In that occasion, we pointed out that no appreciable difficulty had been experienced in effecting the complete replacement of the chlorine atoms with phenyl and *p*-tolyl groups, although the yields of the corresponding *p*-tolyl derivatives were found to be slightly lower. The difference is perhaps due to the greater solubility of the *p*-tolyl compound in several organic solvents and the resulting increase in difficulty of crystallization.

In order to obtain further information on these nucleophilic substitutions, reactions of the mentioned chlorides with *m*-tolyl-magnesium bromide and with the ortho-Grignard compound have been under study during this synthesis period. As we suspected, when *m*-tolylmagnesium bromide is employed the nucleophilic attack on the phosphorus atom becomes more difficult, and it is practically non-existent in yielding completely substituted derivatives with the ortho-Grignard compound. Even with excess of Grignard reagent and upon prolonged refluxing of the reaction mixture, the yields of the compounds obtained from *m*-tolyl-magnesium bromide were found to be very low, and no complete substituted derivative could be isolated when *o*-tolylmagnesium bromide was employed.

We attribute the failure to steric effects which may play an important role in the inhibition of these condensation reactions. Another factor of possible importance is the tendency of the chlorides of pentavalent phosphorus acids to form insoluble complexes with the magnesium halide when treated with Grignard reagents. This tendency is of course increased by steric hindrance. A typical example is shown in the reaction of phosphorus(V) oxytrichloride with organo-magnesium compounds, which yields a mixture of phosphine oxide derivatives together with derivatives of phosphinic acid. The yield of the latter is increased by the use of branched alkyl or aryl groups (2,3).

This complex-forming ability of the intermediates has been encountered in the course of our experiments. After the reaction was completed, product could not be found upon evaporation of the solvent. Furthermore, extraction of the gummy residue with different solvents did not give positive results. The desired compounds could only be separated upon decomposition of the complex with acidic solutions.

This suggests the possibility that with hindered Grignard reagents, the intermediates react with the magnesium halide to give an ethereal insoluble complex which then, under heterogeneous conditions, is no longer capable of reacting with the organo-magnesium compound to yield complete substitution. Upon acidic hydrolysis, however, the complex can be broken, and phosphinic acid derivatives of the type $R_2NSO_2NP(OH)Ar_2$ or $R_2NSO_2NHP(O)Ar_2$ can be obtained.

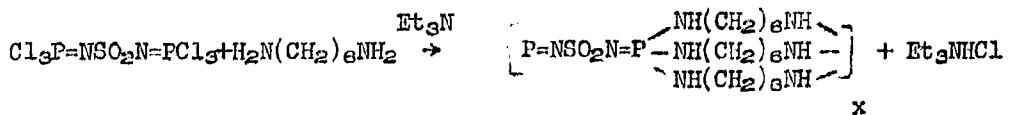
This assumption is also substantiated by the fact that such compounds are soluble in aqueous sodium hydroxide solutions and can be reprecipitated upon acidification at pH ca. 6. The tri-substituted derivatives, by contrast, do not hydrolyze even in boiling aqueous sodium hydroxide.

All the reactions were carried out by slowly adding the chloride to an ether solution of excess Grignard reagent and refluxing for a period of 24 hours after addition was completed. The products were obtained upon hydrolysis of the complex with dilute hydrochloric acid or saturated ammonium chloride. Final purification can be achieved by recrystallization of the crude material from absolute ethanol or dilute ethanol.

III. Reactions of Bis-trichlorophosphazosulfone and of the Dialkylamides of Trichlorophosphazosulfuric Acid with Aliphatic Polyamines.

With the object in view of preparing organic-inorganic polymeric materials, some reactions of bis-trichlorophosphazosulfone and of the dialkylamides of trichlorophosphazosulfuric acid with aliphatic polyamines have been carried out. Although polymerization seems to occur readily when bis-trichlorophosphazosulfone is employed, with *N,N*-diethyl-trichlorophosphazosulfone only monomeric products are formed. The chlorides react vigorously at room temperature when added to a well-stirred solution of 1,6-hexanediamine in benzene in the presence of triethylamine as an acid acceptor.

The compounds obtained, being insoluble in most of the organic solvents, could not be further purified, but analytical data suggest the following stoichiometry:



In the case of the dialkylamides of trichlorophosphazosulfuric acid, the reaction proceeds as follows:



Additional work related to the first type of reaction is necessary in order to establish the nature of this interesting reaction. Some other aliphatic and aromatic polyamines are to be studied in condensation reactions of this type.

IV. Physical Properties

The dialkyl-triarylphosphazosulfones here synthesized are white, crystalline materials, which are insoluble in cold and boiling water; insoluble in diethyl ether, petroleum ether, and *n*-heptane; fairly soluble in ethanol, carbon tetrachloride, and benzene; and soluble in acetone and chloroform. Their purification is best effected by recrystallization from absolute ethanol or dilute ethanol.

The products of the interaction of bis-trichlorophosphazosulfone and of the dialkylamides of trichlorophosphazosulfuric acid with 1,6-hexanediamine are solid, high-melting materials, which are insoluble in the great of organic solvents, in boiling water, and in boiling dimethylformamide, dimethylsulfoxide, and *m*-cresol. For this reason, a good purification could not be achieved, and the products were partially purified by several treatments with boiling water and boiling dimethylformamide.

V. Experimental

A. *N,N*-dimethyl-tri-*m*-tolylphosphazosulfone. Six and fourty-eight

hundreths grams (0.025 mole) of *N,N*-dimethyltrichlorophosphazosulfone in 150 ml. of benzene was slowly added to an ether solution of *m*-tolylmagnesium bromide (19.53 g., 0.1 mole) at room temperature with stirring. After the addition was completed, the reaction mixture was gently refluxed for 24 hours. The excess of Grignard was decomposed by addition of 100 ml. of a saturated aqueous solution of ammonium chloride. The compound was then extracted with benzene. The organic layer was dried over calcium chloride and the excess of solvent removed by distillation under vacuum. The crude product which was left was finally purified by several recrystallizations from ethanol. The pure compound obtained in ca. 10% yield, was a white, crystalline solid which melted at 158-9°C.

Anal. Calcd. for $C_{23}H_{27}N_2O_2PS$: C, 64.77; H, 6.38; N, 6.56
Found: C, 64.91; H, 6.45; N, 6.31

B. *N,N*-morpholine-tri-*m*-tolylphosphazosulfone. Seven and five-tenths

grams (0.025 mole) of *N,N*-morpholinetrichlorophosphazosulfone in 100 ml. of benzene was added at small portions to an ether solution of *m*-tolylmagnesium bromide (19.53 g., 0.1 mole) at room temperature with stirring. The mixture was then refluxed for an additional 24 hrs. after the addition was completed. The reaction product was poured into a flask containing 200 gr. of crushed ice and 50 ml. of 12 M hydrochloric acid. The product was extracted with benzene and the benzene layer dried over calcium chloride. The solid which was left after the removal of the solvent was washed with an aqueous solution of sodium hydroxide, dried, and finally purified by recrystallization from dilute ethanol. The pure compound was a white, crystalline material melting at 123-125°C. obtained in ca. 10% yield.

Anal. Calcd. for $C_{25}H_{29}N_2O_2PS$: C, 64.09; H, 6.24; N, 5.98
Found: C, 64.93; H, 6.44; N, 6.10

C. Attempted Preparation of *N,N*-morpholine-tri-*o*-tolylphosphazosulfone.

Seven and five-tenths grams of *N,N*-morpholinetrichlorophosphazosulfone in 100 ml. of benzene was slowly added at room temperature to a well-stirred ether solution of *o*-tolylmagnesium bromide (19.53 g., 0.1 mole). Gentle refluxing was maintained for 24 hours after the addition was completed. The excess of Grignard reagent was decomposed by pouring the reaction mixture into a flask containing 200 gr. of crushed ice and 50 ml. of 12 M hydrochloric acid. The solid which separated was extracted with benzene and the benzene layer dried over calcium chloride. After the removal of the excess of solvent, the crude product was purified by several recrystallizations

from ethanol. The compound which was obtained, gave m.p. 173-174°C. and microanalysis agrees fairly good for the dirubstituted phosphinic acid derivative.

Anal. Calcd. for $C_{18}H_{22}N_2O_4PS$: C, 54.81; H, 5.87; N, 7.10
Found : C, 56.32; H, 5.87; N, 7.45

D. Reaction between Bis-trichlorophosphazosulfone and 1,6-hexanediamine.

Nine and seventeen-hundredths grams (0.025 mole) of bis-trichlorophosphazosulfone in 50 ml. of benzene, were slowly added at room temperature to a well-stirred solution of 1,6-hexanediamine (11.62 g., 0.1 mole) in 250 ml. of benzene. Some 50 ml. of triethylamine was added to the benzene solution. An insoluble white solid developed as the chloride was added. Stirring at room temperature was continued for additional 6 hours after the addition was completed. The solid was filtered, washed several times with boiling water to remove traces of triethylamine-hydrochloride and subsequently treated with hot dimethylformamide. After drying the product, it melted at 270-280°C. with decomposition.

Anal. Calcd. for $C_{18}H_{42}N_2O_2P_2S$: C, 43.52; H, 8.52; N, 22.57
Found : C, 38.90; H, 8.78; N, 18.21

E. Reaction between N,N -diethyltrichlorophosphazosulfone and 1,6-hexane-

diamine. Seven and eighteen-hundredths grams (0.025 mole) of N,N -diethyltrichlorophosphazosulfone in 50 ml. of benzene was slowly added at room temperature to a stirred solution of 1,6-hexanediamine (11.62 gr. 0.1 mole) in 200 ml. of benzene. Some 50 ml. of triethylamine was added to the benzene solution. After the addition was completed, stirring was continued for additional 6 hours. The solid which was formed was filtered, washed several times with water to dissolve the triethylamine hydrochloride, and finally washed with hot dimethylformamide. The compound so obtained was brown-solid which melted at 255-260°C., with decomposition.

Anal. Calcd. for $C_{28}H_{62}N_{10}O_4P_2S_2$: C, 44.30; H, 8.80; N, 19.0
Found : C, 43.28; H, 8.93; N, 18.74

VI. Discussion

Reactions of the dialkylamides of trichlorophosphazosulfuric acid with *m*- and *o*-tolylmagnesium bromide have shown that steric effects are involved in these nucleophilic substitutions. Steric hindrance becomes most apparent in the reactions with the ortho Grignard compound, where no completely substituted product could be obtained. Instead, probably disubstituted derivatives of phosphinic acid are produced. Polymerization seems to occur readily in reactions of bis-trichlorophosphazosulfone with aliphatic polyamines. Additional work will be undertaken in this field for the synthesis of organic-inorganic polymers.

VII. Outline of Future Work

It is proposed to continue the work outlined in this report. In particular, the reaction of bis-trichlorophosphazosulfone with other aliphatic and aromatic diamines will be investigated extensively. The synthesis of sulfanuric chloride by the Kirsanov procedure, will be studied extensively in order to develop a method that can provide the material in sufficient quantity for further work.

VIII. References

1. T. Moeller and A. Vandi: Quarterly Progress Report No. 9, Contract DA-11-022-2956, August 31, 1961.
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3. K. A. Petrov, N. K. Bliznyuk, and U. P. Korotkova, J. Gen. Chem. U.S.S.R., 30, 2967 (1960).